Field-induced layer thinning transition on free-standing smectic films

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Strongly anchored free-standing smectic films usually present a stepwise reduction of the number of layers when the temperature is raised above the smectic-isotropic bulk transition temperature. Here, we demonstrate that a field-induced layer thinning transition can take place in smectic films with a negative dielectric anisotropy even below the bulk transition temperature. Using an extended McMillan's model, we provide the phase diagram of this layering transition and show that, when the field is raised above the bulk transition field, the film thickness reduction is well described by a power-law with an exponent that depends on the temperature and the aspect ratio of the liquid crystal molecule.

Surface and external field effects on the liquid crystal properties have attracted an appreciable interest over the past decade, being the subject of several theoretical and experimental works [1, 2, 3, 4, 5, 6]. In particular, these systems exhibit a rich phenomenology associated with the surface anchoring, as well as with the coupling between orientational order and electric or magnetic fields [7]. In fact, surface ordering and field-induced reorientation are essential mechanisms to understand a great variety of problems involving liquid crystals in different areas, such as phase transitions, nonlinear optics, and colloidal dispersions.

It is well known that surface effects may stabilize the smectic order in free-standing films well above the bulk transition temperature [8]. Depending on the strength of the surface anchoring, several unusual phenomena may be observed in such systems. A prominent example of surface-induced phenomenon is the layer thinning transition in free-standing smectic films which consists in a stepwise reduction of the film thickness as the temperature is raised above of the bulk transition temperature [9]. By using the optical reflectivity technique, experimental works have observed the layer thinning transition in a large variety of compounds [9, 10, 11, 12, 13, 14, 15]. In all cases, the film thickness reduction was suitably described by a simple power-law expression $N(t) \propto t^{-\nu}$, where N is the number of layers and t is the reduced temperature. However, it was noticed that the exponent ν assumes values in the range $0.52 \leq \nu \leq 0.82$ for different compounds. Recent theoretical investigations have demonstrated that the main experimental characteristics of the thinning transitions can be understood in the light of mean-field models [16, 17, 18]. In particular, the experimental range of the thinning exponent was reproduced by varying some typical parameters of the models, as the surface anchoring [17] and the interaction strength for the smectic-A phase [18].

Recently, the effects of an external field on the liquid crystal phase transitions have been systematically investigated. In particular, experimental studies have reported that an external field may promote the emergence of ordered phases well above the isotropic-nematic and isotropic-smectic bulk transition temperatures [4, 19]. Close to the nematic - smectic A transition, birefringence measurements revealed that a strong electric field suppresses the nematic fluctuations in systems with a positive dielectric anisotropy, resulting in a field-driven crossover from first to second order phase transition [5]. An inverse crossover has also been identified in the Fréederichsz transition in thin homeotropic cells of a liquid crystal with a negative dielectric anisotropy [6]. In free-standing smectic films, an optical field was observed to induce a layer thickening in photosensitive samples [20]. Further, theoretical investigations have predicted that a magnetic field may affect the layering transition, enhancing the transition temperature of films with a positive diamagnetic susceptibility anisotropy [21]. However, the possibility of a controlled reduction of the film thickness by an external field has not been explored so far. Such phenomenon would establish a new theoretical and experimental ground to study the joint surface and field effects on the liquid crystal order and its dimensional reduction.

In the present letter, we demonstrate that a field-induced layer thinning transition can indeed take place in free-standing smectic films even below to smectic-isotropic bulk transition temperature. We will use an extended McMillan model to explicitly take into account the discrete layered structure and the surface anchoring energy of thin smectic films. For strongly anchored films with a negative dielectric anisotropy, we will show that the external electric field induces a power-law stepwise reduction of the film thickness similar to the standard temperature-induced thinning transition. This phenomenon contrasts with the field-enhanced order predicted to occur in films with positive anisotropy[21]. Further, we will characterize the dependence of the effective power-law exponent with the temperature and the aspect ratio of the liquid crystal molecule.

A free-standing smectic film is described as a stack of smectic layers confined by a surrounding gas [7]. Due to strong surface interactions, the molecular alignment tends to be normal to the layer's plane and the film can be considered as a smectic monodomain. Nevertheless,

an electric field perpendicular to the layer's plane may induce a molecular reorientation in systems with a negative dielectric anisotropy. In a mean-field approach for a film with N discrete layers, the effective potential felt by a molecule located at the i-th smectic layer can be written as [16]:

$$V_1(z_1, \theta_1) = -\frac{V_0}{3}\left[s_1 + s_2 + 3W_0/V_0 + \varepsilon_a^* E^2/V_0 \right. \\ \left. + \alpha \cos(2\pi z_1/d)(\sigma_1 + \sigma_2)\right] P_2(\cos\theta_1) \quad (1)$$

$$V_i(z_i, \theta_i) = -\frac{V_0}{3}\left[\sum_{j=i-1}^{i+1} s_j + \varepsilon_a^* E^2/V_0 \right. \\ \left. + \alpha \cos(2\pi z_i/d)\left(\sum_{j=i-1}^{i+1}\sigma_j\right)\right] P_2(\cos\theta_i) (2)$$

$$V_N(z_N, \theta_N) = -\frac{V_0}{3}\left[s_N + s_{N-1} + 3W_0/V_0 + \varepsilon_a^* E^2/V_0 \right. \\ \left. + \alpha\cos(2\pi z_N/d)(\sigma_N + \sigma_{N-1})\right]P_2(\cos\theta_N)(3)$$

Here, $P_2(cos\theta_i)$ is the second-order Legendre polynomial with θ_i being the angle between the long axis of a molecule at the i-th layer and the z direction. s_i and σ_i are the orientational and translational order parameters in the i-th layer, respectively. V_0 is a parameter of the microscopic model that determines the scale of the nematic-isotropic transition temperature [22]. The parameter α is related to the length of alkyl chains of calamitic molecules through the expression $\alpha = 2exp[-(\pi r_0/d)^2]$, where r_0 is a characteristic length associated to the length of the molecular rigid section, and d is the smectic layer spacing. The parameter W_0 corresponds to the strength of the homeotropic surface anchoring which is assumed to be short ranged. E represents an external electric field which is applied perpendicularly to the layer plane. ε_a^* is defined as $\varepsilon_a^* = \varepsilon_a/4\pi n_0$, where ε_a is the dielectric anisotropy of the system and n_0 is the density of particles. In liquid crystal samples with positive dielectric anisotropy, an external electric field tends to reinforce the nematic and smectic order parameters. However, in compounds with negative anisotropy ε_a, a perpendicular electric field reduces the smectic order through the reorientation of the molecular alignment. It is this scenario that we will explore in what follows, concerning the possibility of field-controlled reduction of the film thickness.

The local order parameters s_i and σ_i satisfy the self-consistent equations:

$$s_i = \langle P_2(cos\theta_i)\rangle_i \quad (4)$$

and

$$\sigma_i = \langle P_2(cos\theta_i)cos(2\pi z_i/d)\rangle_i, \quad (5)$$

with the thermodynamical averages being computed from the one particle distribution function in the i-th smectic layer, given by

$$f_i(z_i, \theta_i) \propto exp\left[-V_i/k_B T\right] \quad , \quad (6)$$

where k_B is the Boltzmann constant and T is the temperature. The solutions of Equations (4) and (5) minimize the total Helmholtz free-energy [18]. In the absence of an external electric field, this model predicts a similar McMillan's phase diagram for the internal layers when the film thickness l is much larger than the surface penetration length δ [23]. In particular, we will restrict the present work to this limit ($l >> 2\delta$). Also, we will consider only cases for which $\alpha > 0.98$ which corresponds to compounds that present a first order smectic-isotropic phase transition according to the McMillan's mean field approach. In this regime, the self-consistent equations exhibit two locally stable solutions, corresponding to a smectic phase and a melted center phase which has a null smectic order near the film center[18]. The equilibrium state is determined from the global minimum of the Helmholtz free-energy.
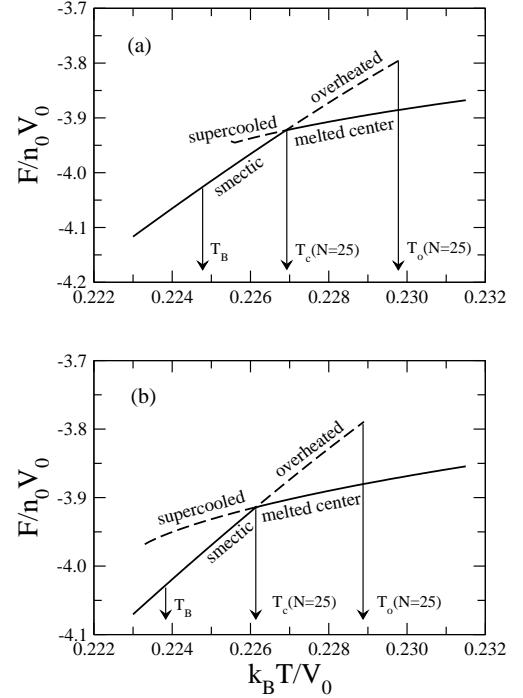

FIG. 1: Helmholtz free-energy as a function of temperature for the solutions of the self-consistent equations which are locally stable. The model parameters are $N = 25$, $W_0 = 2.5\,V_0$, and $\alpha = 1.05$. (a) $\sqrt{|\varepsilon_a^*|/V_0}E = 0$ and (b) $\sqrt{|\varepsilon_a^*|/V_0}E = 0.12$. Solid lines represent the global stable solution and dashed lines correspond to supercooled and overheated states. Notice that the external field reduces the transition temperature $T_c(N)$ associated with the melting of the central layers, as well as the bulk transition temperature T_B and the limiting temperature $T_o(N)$ above which the overheated phase becomes unstable.

In Fig.1 we present the Helmholtz free-energy as a function of the temperature for the locally stable solu-

tions of the self-consistent relations. The model parameters used were $N = 25$, $W_0 = 2.5V_0$, and $\alpha = 1.05$, which corresponds to a zero-field bulk transition temperature of $T_B = 0.22482V_0/k_B$. At zero field, a film with N layers exhibits a transition temperature $T_c(N)$ at which the film center melts. For $N = 25$, we obtain $T_c(N = 25) = 0.22695V_0/k_B$, as shown in Fig.1(a). Above $T_c(N)$, the solution with a non-null smectic order in the center of the film corresponds to a metastable overheated smectic phase. The equilibrium solution above $T_c(N)$ is the melted center one. Below $T_c(N)$, a metastable supercooled melted center phase can be reached, although the equilibrium solution is the smectic phase. Both metastable solutions only appear in a finite temperature range around $T_c(N)$, as expected near a first-order transition. In the presence of an external electric field, we notice that the transition temperature is shifted to a lower value, as shown in Fig.1(b). Here, we used $\sqrt{|\varepsilon_a^*|/V_0}E = 0.12$. Further, we notice an enhancement in the range of temperatures at which the supercooled isotropic phase is locally stable.
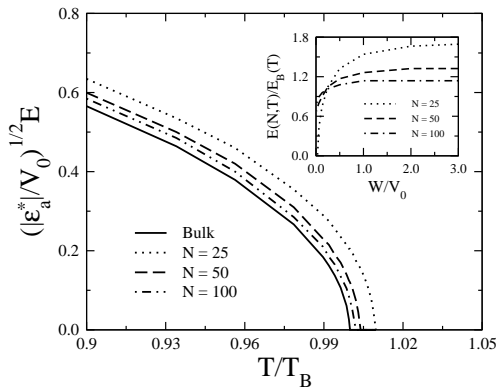

FIG. 2: Phase diagram in the $E \times T$ parameter space for $\alpha = 1.05$, $W_0 = 2.5\ V_0$, and several film thicknesses. In this strong anchoring regime, the transition temperature increases as the film thickness reduces. Here T_B is the zero-field bulk transition temperature. The inset shows the transition field as a function of the surface anchoring for $T = 0.2230\ V_0/k_B$ and distinct film thicknesses. The crossing point delimits the weak and strong anchoring regimes.

The phase diagram showing the field dependence of the transition temperature for films with distinct thicknesses is reported in Fig.2, for the particular case of $W_0 = 2.5\ V_0$ and $\alpha = 1.05$. The bulk phase diagram is also exhibited. We can observe that the transition temperature is higher for thin films under such strong surface anchoring. Further, the molecular reorientation promoted by the external field reduces the transition temperature. The inset shows the transition field as a function of the surface anchoring for several film thicknesses for $T = 0.2230\ V_0/k_B$, which is below the zero-field bulk transition temperature. The curves crosses roughly at a common point which delimits two anchoring regimes. Below the crossing point, the transition field increases with the film thickness, thus
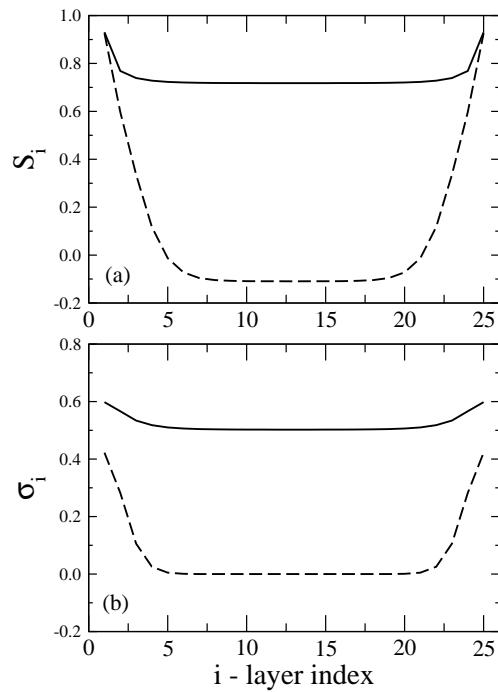

FIG. 3: Profiles of the (a) nematic and (b) smectic order parameters for different external fields: $\sqrt{|\varepsilon_a^*|/V_0}E = 0.270$ (solid lines) and $\sqrt{|\varepsilon_a^*|/V_0}E = 0.275$ (dashed lines). Here, $T = 0.2230\ V_0/k_B$, $N = 25$, and $W_0 = 2.5\ V_0$. The zero-field bulk transition temperature is $T_B = 0.22482V_0/k_B$. Notice the field-induced discontinuous transition from the state with finite nematic and smectic order parameters to the melted state at the film center.

leading to the melting of the entire film. On the other hand, the transition field is larger for thin films in the strong surface anchoring regime. Therefore, the field-induced transition in this regime corresponds to the melting of inner layers, as illustrated in Fig.3. In contrast with a null smectic order parameter near the film center, the nematic order parameter becomes negative which reflects the field-induced reorientation of the molecular alignment [24]. The melting of the central layers in the regime of strong surface anchoring is the typical scenario leading to the layer thinning phenomenon.

In the absence of an external field, the layer thinning transition corresponds to a stepwise power-law reduction of the film thickness as the temperature is raised above the bulk transition temperature [9, 18]. The above results indicate that a similar layer thinning transition can take place below the bulk transition temperature with the film thickness controlled by an external field. In Fig. 4 we exhibit the field dependence of the film thickness for distinct values of the temperature in the regime of strong surface anchoring. One can notice a continuous thinning of the film thickness as the external field exceeds the bulk transition field. Such behavior can be reasonably described by a power law $N(E) \propto [E(T) - E_B(T)]^{-\nu}$, where $E_B(T)$ is the bulk transition field. The different
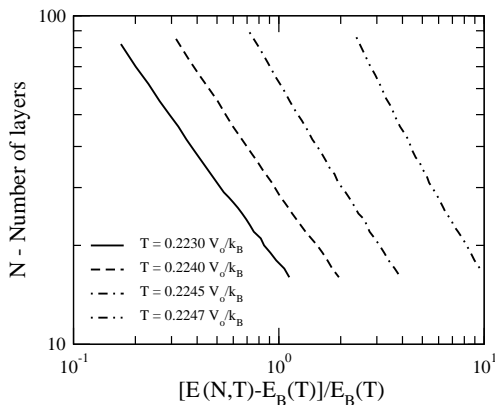
FIG. 4: External field dependence of the film thickness for different values of the temperature. We used $\alpha = 1.05$ and $W_0 = 2.5\,V_0$. $E_B(T)$ is the bulk transition field at temperature T. In the thickness range shown, the thinning transition follows closely a power law dependence with the reduced external field $E(T) - E_B(T)$.
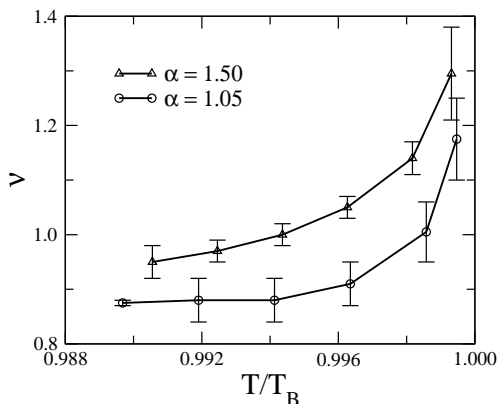

FIG. 5: Temperature dependence of the characteristic exponent ν of the field-induced layer thinning transition for $W_0 = 2.5\,V_0$. The error bars account for the small variability of the exponent along the transition line in the range of film thicknesses shown in Fig. 4. The exponent ν increases monotonically as the bulk transition temperature is approached.

slopes of the curves point to a slight temperature dependence of the exponent ν. Fig. 5 shows that the power-law exponent ν is smaller than unity far from the bulk transition temperature. These values are of the same order of magnitude of those observed in temperature-induced layer thinning transitions [18]. However, ν becomes larger close to the bulk transition temperature. Further, we notice that power-law exponent depends on the parameter α, which is related to the length of the alkyl chains of the liquid crystal molecules. The reduction of the film thickness is faster in liquid crystal compounds with longer alkyl chains.

In summary, we demonstrated that a layer thinning transition can be induced by an external electric field in free standing smectic films, under strong surface anchoring and below the bulk transition temperature. We considered a system with a negative dielectric anisotropy on which an external field perpendicular to the layer plane can promote a Fréedericksz transition in the center of the film. The reorientation of the molecular alignment is accomplished by the melting of the inner smectic layers thus leading to the layer thinning transition. Our results showed that the number of smectic layers decays monotonically with the external field. In the range of film thicknesses investigated, the reduction in the number of layers is well described by a power-law $N(E) \propto [E(T) - E_B(T)]^{-\nu}$ above the field $E_B(T)$ that is able to reorient bulk samples at temperature T. The effective exponent ν increases as the temperature approaches to the bulk transition temperature. Further, our results indicated that the effective exponent ν is larger in compounds with longer alkyl chains. Considering the typical liquid crystal physical parameters, the presently predicted field-induced layer thinning transition can be experimentally observed for electric fields of the order of 10^5 V/cm, which is well within achievable values [5, 6]. Efforts in this direction would bring valuable information concerning the interplay of field, surface and finite-size effects in the phase transitions depicted by free-standing smectic films.

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